Palladium-Catalyzed Reaction of 5-Methylene-1,3-dioxolan-2-ones. A New Access to and Reactivity of Oxatrimethylenemethane–Palladium

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The oxidative addition of 5-methylene-1,3-dioxolan-2-ones (1) to a low-valent palladium complex and the subsequent decarboxylation has been studied as an access to oxatrimethylenemethane–palladium (OTMM–Pd) intermediates in a catalytic process. The reaction of 5,5-dimethyl-4-methylene-1,3-dioxolan-2-one (**1a**) with norbornene in the presence of $Pd(PPh_3)_4$ gave 3-(2-methylpropanoyl)tricyclo[3.2.1.$0^{2,4}$]octane (**3a**) via addition and isomerization. In the catalytic reaction of **1a** with several isonitriles, insertion of two molecules of the isonitrile into OTMM intermediate **2a** took place to give 2-iminofurans **11**. Similarly, the carbonate **1a** reacted with aromatic isocyanates to give the corresponding oxazolidinones **12** as a result of [3 + 2] cycloaddition. The reaction of **1a** with trimethylsilyl cyanide gave cyanated silyl enol ether **17**. The zwitterionic character of OTMM–Pd seems to explain this reactivity.

Introduction

Advantage has been taken of the coordination of transition metals to stabilize reactive intermediates, such as carbene, cyclobutadiene, trimethylenemethane (TMM), and so on. There is also much that can be learned by the preparation of new transition-metal complexes of otherwise unstable and highly reactive chemical species.[1] The carbene complexes have shown widespread utility for organic synthesis,[2] and the introduction of the TMM–palladium complex by Trost has provided fruitful chemistry in the cycloaddition constructing cyclopentane skeletons.[3] Recently transition-metal complexes of heterotrimethylenemethanes such as oxatrimethylenemethane,[4] silatrimethylenemethane,[5] and thiatrimethylenemethane[6] have been investigated from the point of view of their structural interest and synthetic utility. We have previously demonstrated the utility of 4-methyleneoxazolidin-2-ones as precursors of azatrimethylenemethane–palladium complexes which are intermediates in catalytic reactions.[7] In this paper we report the utility of cyclic carbonates for the generation of an oxatrimethylenemethane–palladium (OTMM–Pd) intermediate and the results of a series of palladium-catalyzed reactions involving OTMM–Pd. Our approach to OTMM–Pd (Scheme I) involves the reaction of 1 with Pd(0) leading to 2 via oxidative addition and subsequent decarboxylation.[8] A theoretical and structural study of OTMM-d^{10}–metal complex has shown a η^3-mode with zwitterionic character for the OTMM ligand.[4a] On the basis of this zwitterionic character of the OTMM–Pd complex, the details of our research into its catalytic activity are presented here.

Scheme I

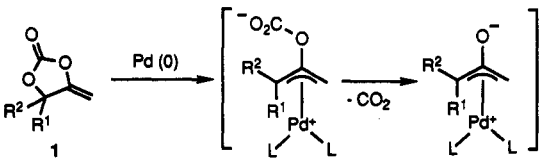
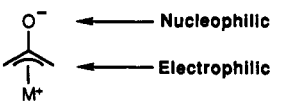


Chart I



Results and Discussion

Reaction of 5,5-Dimethyl-4-methylene-1,3-dioxolan-2-one (1a) with Norbornenes Leading to Cyclopropanation. The reaction 5,5-disubstituted 4-methylene-1,3-dioxolan-2-ones **1a–d** with norbornene (1:2 molar ratio) in the presence of 5 mol % $Pd(PPh_3)_4$ took place in toluene at reflux for 15 h to give [2 + 1] cycloaddition products **3a–d** in good yields (eq 1). These results obtained here

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(2) For recent review, see: Wulff, W. D. In *Advances in Metal–Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1989; Vol. 1, pp 209–393.

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(8) The related intermediate have been reported: Inoue, Y.; Ohuchi, K.; Yen, I.-F.; Imaizumi, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3518. Inoue, Y.; Ohuchi, K.; Imaizumi, S.; Hagiwara, H.; Uda, H. *Synth. Commun.* **1990**, *20*, 3063. Joumier, J. M.; Bruneau, C.; Dixneuf, P. H. *Synlett* **1992**, 453.

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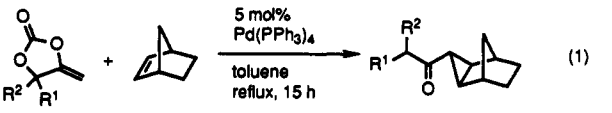
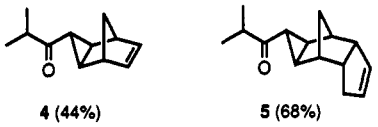


(1)

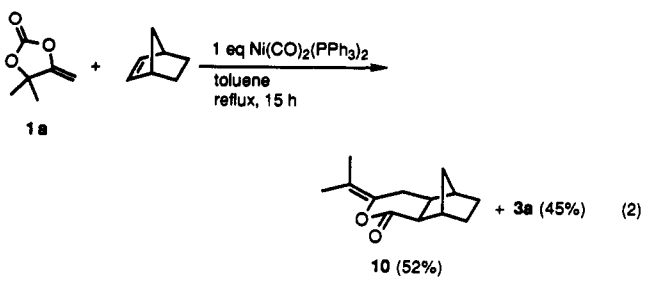
1a; $R^1 = R^2 = Me$ — 3a (86%)
1b; $R^1 = Me$, $R^2 = Ph$ — 3b (100%)
1c; $R^1 = Me$, $R^2 = CH_2CH_2CH{=}CH_2$ — 3c (83%)
1d; $R^1, R^2 = -(CH_2)_5-$ — 3d (48%)

are in line with the cyclopropanation reactions reported previously in the palladium-catalyzed reaction of 4-methyleneoxazolidin-2-one with norbornenes[7] and in that of bifunctional conjunctive reagents, 1-acetoxy-3-(trimethylsilyl)propan-2-one[4k] and methyl 2-(trimethylsiloxy)prop-2-enylcarbonate.[4l] Thus, these results suggest that methylenedioxolan-2-one (1) can serve as a precursor to OTMM–Pd 2. The reactions of 1a with norbornadiene and dicyclopentadiene using a 1:2 molar ratio afforded the cyclopropanation products 4 and 5 in 44 and 68%



4 (44%) 5 (68%)

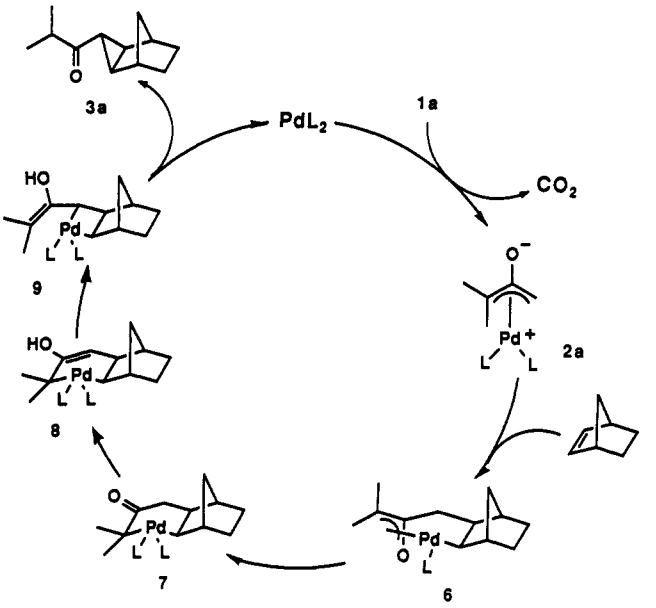
yields, respectively, without formation of double cyclopropanation products. In all reactions with norbornenes tested no endo products were obtained. In the case of the reaction of 1a with dicyclopentadiene, only the double bond in the norbornane skeleton was cyclopropanated. Reactions of 1a with styrene and methyl acrylate under the same reaction conditions gave no cycloaddition products. $Pd(PPh_3)_4$ was found to be the best catalyst, whereas $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$, $RhH(CO)(PPh_3)_3$, $Rh_6(CO)_{16}$, and $Pt(PPh_3)_4$ were not effective. The use of a stoichiometric amount of $Ni(cod)_2/PPh_3$ (1:3) promoted the reaction of 1a with norbornene to produce the same product 3a in 66% yield. Trost reported that $Pd_2(dba)_3{\cdot}CHCl_3/PPh_3$ was effective as a catalyst for the reaction of 1-acetoxy-3-(trimethylsilyl)propan-2-one with norbornene.[4k] In the present system, however, the use of this catalyst resulted in a low conversion (30%) of 1a giving 3a in 16% yield even after 60 h. Scheme II shows a plausible reaction mechanism, which has been similar to that proposed by Trost. The cyclopropanation described here seems to proceed via addition of 2a to norbornene followed by the isomerization, which involves a proton shift (7 → 8) and a 1,3-Pd shift (8 → 9). Interestingly, the reaction of 1a with norbornene in the presence of a stoichiometric amount of $Ni(CO)_2(PPh_3)_2$ afforded a lactone 10 (52%) in addition to 3a (45%) (eq 2). The



(2)

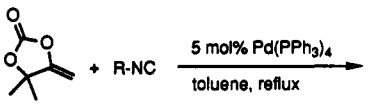
formation of 10 can be interpreted as the result of the interception of the intermediate similar to 6 by carbon monoxide coordination to the metal. A similar reaction

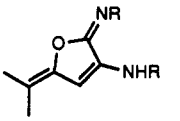
Scheme II



using a catalytic amount of $Pd(PPh_3)_4$ under an ambient or slightly higher pressure (20 kg/cm^2) of carbon monoxide did not give 10; 1a was recovered.

Reaction of 1a with Isonitrile. Interestingly, when isonitrile was used in place of carbon monoxide, we encountered the incorporation of two molecules of the isonitrile into the OTMM unit to produce an iminofuran derivative. On treatment of 1a with *tert*-butyl isocyanide in the presence of 5 mol % $Pd(PPh_3)_4$ in toluene at 110 °C for 15 h, 5-isopropylidene-3-(*tert*-butylamino)-2-(*tert*-butylimino)-2,5-dihydrofuran (11a) was obtained in 26% yield (eq 3). The carbonate 1a also reacted catalytically





(3)

11a 26% (R = ^{t}Bu, 15 h)
11b 49% (R = 2,6-xylyl, 28 h)
11c 54% (R = 2,6-diethylphenyl, 24 h)

with the aromatic isonitriles, 2,6-xylyl isocyanide and 2,6-diethylphenyl isocyanide, to give 11b (49% yield) and 11c (54% yield), respectively. The formation of 11a–c might be regarded as the result of the well-known successive insertion[9] of isonitriles into the carbon–palladium bond of the π-allyl species 2a. The another possibility may involve the reductive coupling via a cyclic diiminopalladium complex. The isonitrile insertion reaction can be referred to as a net [3 + 1 + 1] cyclocoupling of OTMM and two molecules of isonitrile.

Reaction of 1a with Heterocumulenes. The OTMM–Pd 2 may be regarded as an unusually substituted

(9) The successive insertions of isonitriles into methylpalladium have been known: Ostuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196. Yamamoto, Y.; Yamazaki, H.; *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2653. See also Pd-catalyzed poly-insertion of isonitriles: Ito, Y.; Ihara, E.; Murakami, M. *J. Am. Chem. Soc.* **1990**, *112*, 6446. Onitsuka, K.; Joh, T.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 851.

Scheme III

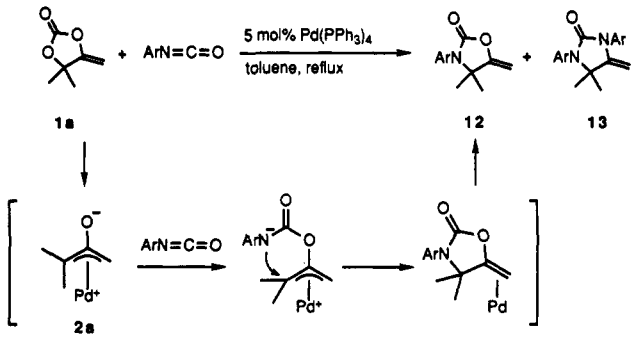
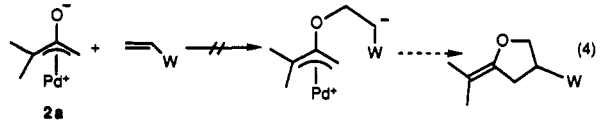


Table I. The Pd-Catalyzed Reaction of 1a with Aromatic Isocyanates[a]

Ar in ArNCO	time, h	isolated yield, %	
C_6H_5	8	**12a**, 78	**13a**, 19
p-MeC_6H_4	8	**12b**, 79	**13b**, 16
p-$MeOC_6H_4$	9	**12c**, 64	**13c**, 12
p-ClC_6H_4	7	**12d**, 58	**13d**, 12
p-$NO_2C_6H_4$	4	**12e**, 90	**13e**, 7

[a] **1a** (2.0 mmol) and ArNCO (2.2 mmol) in the presence of $Pd(PPh_3)_4$ (0.1 mmol) were under reaction conditions of toluene (5 mL) at reflux temperature under nitrogen.

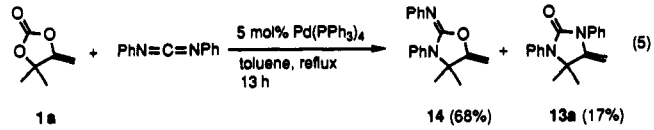
(π-allyl)palladium. Various attempts for cycloaddition of **2** with an olefin bearing an electron-withdrawing group were unsuccessful probably because of the lower nucleophilicity of the oxygen anion of **2** (eq 4). In search of a



(4)

[3 + 2] cycloaddition, reactions of a series of heterocumulenes were examined. The palladium-catalyzed reaction of **1a** with aromatic isocyanates underwent cycloaddition to give the corresponding carbamates **12** in good yields together with cyclic ureas **13** (Scheme III). Typical results are listed in Table I. Other carbonates **1b** and **1c** also reacted with phenyl isocyanate to give similar products **12f** (33%) and **12g** (68%), respectively (see Experimental Section). The formation of **12** is accounted for by assuming the intramolecular attack of a nitrogen anion, initially formed by the attack of an oxygen anion of OTMM–Pd to an isocyanate, at the more hindered carbon of a π-allyl palladium moiety. The regioselectivity of the reaction is ascribed to the thermodynamic stability of the olefin–palladium complex appearing in the last step. The mechanism for byproduction of **13** is not clear. The conversion of **12a** to **13a** was not observed in the reaction of **12a** with phenyl isocyanate under these reaction conditions. The reactions of **1a** with diphenyl carbodiimide and diphenyl ketene resulted in a net [3 + 2] cycloaddition to produce iminooxazolidine **14** (68% yield) and benzhydridenedioxolane **15** (44% yield), respectively (eqs 5 and 6). In the former reaction, byproduct **13a** was also obtained, whereas in the latter case *C*-cyclization product **16** was obtained as a byproduct.

Reaction of 1a with Silylated Nucleophiles. We examined the reaction of **1a** with some silylated nucleophiles relying upon the oxophilicity of silyl groups. The reactions of **1a** with trimethylsilyl cyanide in the presence of the palladium catalyst resulted in the formation of **17** in 62% yield (eq 7). The attack of cyanide occurred at the



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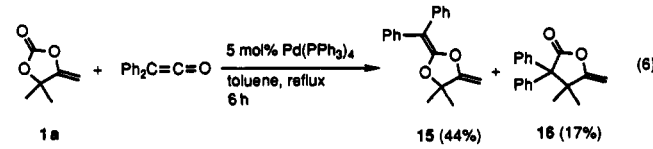
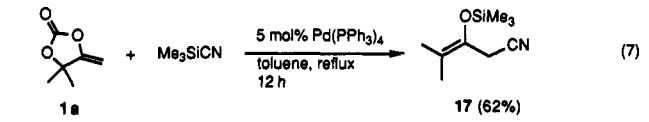


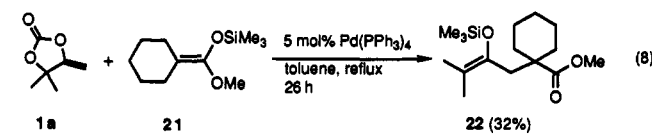
(6)

less hindered side of the (π-allyl)palladium complex. The steric congestion of the intermediate (π-2-siloxyallyl)palladium species might have determined the regioselectivity

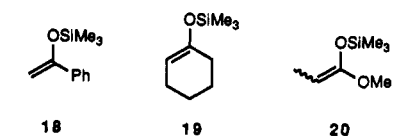


(7)

of the reaction. The results obtained here suggest that the OTMM–Pd (**2**) functionality has a zwitterionic character. The reaction with the trimethylsilyl enol ethers of acetophenone and cyclohexanone (**18** and **19**, respectively) and with the ketene trimethylsilyl acetal of methyl propionate (**20**) did not take place. However, the reaction of **1a** with the ketene silyl acetal of methyl cyclohexanecarboxylate (**21**) resulted in the formation of **22** in 32% yield (eq 8). It is noted that the reaction with only a β,β-



(8)



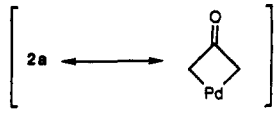
disubstituted ketene silyl acetal occurred to give the product. The differences in the reactivities of silyl compounds examined in this reaction cannot be rationalized at present, but it seems that the reaction giving **22** involves a one-electron transfer mechanism[10] rather than an ionic one.

Conclusion

The OTMM–Pd species which can be generated by oxidative addition and decarboxylation of cyclic carbonate **1** exhibited versatile reactivities in several catalytic reactions. These results obtained here suggest that the OTMM–Pd possesses a zwitterionic character but the nucleophilicity of the oxygen anion OTMM–Pd is rather low. The low nucleophilicity may be due to the contribution of a resonance stracture in which delocalization of the negative charge on the oxygen atom in a manner to form a carbonyl double bond of a η^2-palladacyclobutanone structure (**23**) take place.

(10) Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H.; Fukuzumi, S. *J. Am. Chem. Soc.* **1991**, *113*, 4028.

Chart II



23

Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) spectrometer. GLC analyses were performed with 25-m × 0.2-mm CBP1-M25-025 capillary column.

Materials. Unless otherwise noted, materials were obtained commercially and were purified by distillation or recrystallization. Cyclic carbonates **1a–d** were prepared by the reported methods.[11] Aromatic isonitriles,[12] diphenylcarbodiimide,[13] diphenyl ketene,[14] trimethylsilyl enol ethers **19** and **20**,[15] and trimethylsilyl ketene acetals **21** and **22**[16] were prepared according to the previous procedures.

General Procedure for the Pd-Catalyzed Reaction of Cyclic Carbonate 1a with Norbornenes. 3-(2-Methylpropanoyl)tricyclo[3.2.1.0^{2,4}]octane (3a). In a flame-dried 10-mL two-necked flask fitted with a condenser and rubber septum were placed $Pd(PPh_3)_4$ (0.115 g, 0.1 mmol) and a magnetic stirring bar under nitrogen. To toluene (3 mL) was successively added a solution of 5,5-dimethyl-4-methyleneoxolan-2-one (**1a**) (0.256 g, 2.0 mmol) and norbornene (0.377 g, 4.0 mmol) in toluene (2 mL) by syringe. The contents of the flask were stirred at room temperature until all components were dissolved. The solution was stirred at reflux temperature for 15 h. After cooling, the mixture was filtered with Celite. Evaporation of the solvent under reduced pressure left an orange oil, which was subjected to column chromatography on SiO_2 using hexane/ethyl acetate (10:1) as an eluent to give 0.306 g (1.72 mmol, 86% yield) of pure **3a** as a white solid: mp 60–64 °C; ^1H NMR ($CDCl_3$) δ 0.72 (d, J = 10.8 Hz, 1 H), 0.98 (dt, J = 10.8, 2.3 Hz, 1 H), 1.10 (d, J = 6.9 Hz, 6 H), 1.31 (dd, J = 7.7, 2.3 Hz, 2 H), 1.33 (d, J = 2.1 Hz, 2 H), 1.46 (d, J = 7.7 Hz, 2 H), 1.91 (t, J = 2.3 Hz, 1 H), 2.35 (br s, 2 H), 2.69 (sep, J = 6.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.6, 22.9, 28.8, 29.0, 29.2, 36.3, 42.1, 214.2; IR (KBr) 1684 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.89; H, 10.40.

3-(2-Phenylpropanoyl)tricyclo[3.2.1.0^{2,4}]octane (3b): yield 100%; a white solid; 40–42 °C; ^1H NMR ($CDCl_3$) δ 0.60 (d, J = 10.7 Hz, 1 H), 0.78 (ddd, J = 10.7, 2.0, 2.0 Hz, 1 H), 1.22–1.31 (m, 4 H), 1.31 (m, 1 H), 1.36 (d, J = 7.0 Hz, 3 H), 1.41 (m, 1 H), 1.80 (dd, J = 2.4, 2.4 Hz, 1 H), 2.15 (d, J = 2.0 Hz, 1 H), 2.86 (d, J = 2.0 Hz, 1 H), 3.83 (q, J = 7.0 Hz, 1 H), 7.17–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.7, 23.8, 28.5, 28.6, 29.3, 36.0, 53.8, 126.8, 127.9, 128.7, 141.0, 210.1; IR (KBr) 1696 (C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.82; H, 8.61.

3-(2-Methyl-1-hexenoyl)tricyclo[3.2.1.0^{2,4}]octane (3c): 83% yield; colorless liquid; ^1H NMR ($CDCl_3$) δ 0.70 (d, J = 10.7 Hz, 1 H), 0.96 (d, J = 10.7 Hz, 1 H), 1.07 (d, J = 6.8 Hz, 3 H), 1.28–1.38 (m, 4 H), 1.41–1.47 (m, 2 H), 1.36–1.41 (m, 1 H), 1.70–1.84 (m, 1 H), 1.88 (t, J = 2.3 Hz, 1 H), 2.03 (dt, J = 7.4, 7.4 Hz, 2 H), 2.34 (br s, 2 H), 2.61 (tq, J = 6.8, 6.8, 1 H), 4.96 (dd, J = 1.7, 10.3 Hz, 1 H), 5.01 (dd, J = 1.7, 17.0 Hz, 1 H), 5.78 (ddt, J = 17.0, 10.3, 7.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.2, 23.1, 28.5, 28.6, 28.8, 31.4, 32.0, 35.9, 46.5, 114.8, 138.1, 213.5; IR (neat) 1696 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.56; H, 10.15.

3-(Cyclohexylcarbonyl)tricyclo[3.2.1.0^{2,4}]octane (3d): 48% yield; a white solid; 81–83 °C: ^1H NMR ($CDCl_3$) δ 0.69 (d, J = 10.5 Hz, 1 H), 0.96 (d, J = 10.5 Hz, 1 H), 1.25–1.37 (m, 10 H), 1.44 (m, 2 H), 1.80 (m, 4 H), 1.90 (t, J = 2.4 Hz, 1 H), 2.33 (br s, 2 H), 2.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.8, 25.7, 25.9, 28.4, 28.5, 28.7, 28.9, 36.0, 51.8, 213.3; IR (KBr) 1684 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.44; H, 10.41.

3-(2-Methylpropanoyl)tricyclo[3.2.1.0^{2,4}]-6-octene (4): 44% yield; a white solid; mp 31–33 °C: ^1H NMR ($CDCl_3$) δ 1.02 (d, J = 9.2 Hz, 1 H), 1.11 (d, J = 7.0 Hz, 6 H), 1.21 (d, J = 9.2 Hz, 1 H), 1.61 (m, 2 H), 2.67 (sep, J = 7.0 Hz, 1 H), 2.90 (br s, 2 H), 2.90 (m, 2 H), 6.40 (br s, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.2, 34.0, 38.6, 40.2, 41.3, 42.0, 140.9, 211.2; IR (KBr) 1700 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.60; H, 9.01.

9-(2-Methylpropanoyl)tetracyclo[5.3.1.0^{2,6}.0^{8,10}]-3-undecene (5): 68% yield; colorless liquid; ^1H NMR ($CDCl_3$) δ 0.94 (d, J = 9.7 Hz, 1 H), 1.08 (d, J = 7.3 Hz, 6 H), 1.12 (m, 1 H), 1.18 (d, J = 9.7 Hz, 1 H), 1.48 (m, 1 H), 1.99 (m, 1 H), 2.3–2.4 (m, 1 H), 2.32 (m, 2 H), 2.3–2.5 (m, 1 H), 2.57 (m, 1 H), 2.68 (sep, J = 7.3 Hz, 1 H), 3.10 (m, 1 H), 5.52 (m, 1 H) 5.72 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.3, 21.8, 23.6, 26.7, 31.4, 31.7, 38.4, 39.7, 41.8, 42.9, 54.6, 130.0, 132.7, 214.0; IR (neat) 1700 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{20}O$: C, 83.33; H, 9.26. Found: C, 82.81; H, 9.35.

General Procedure for the Pd-Catalyzed Reaction of 1a with Isonitrile. 11b (R = 2,6-Xylyl). In a flame-dried 10-mL two-necked flask fitted with a condenser and rubber septum were placed $Pd(PPh_3)_4$ (0.115 g, 0.1 mmol) and a magnetic stirring bar under nitrogen. To toluene (5 mL) were successively added **1a** (0.256 g, 2.0 mmol) and 2,6-xylyl isocyanide (0.524 g, 4.0 mmol) by a syringe. The solution was stirred at reflux temperature for 28 h. After cooling, the mixture was filtered with Florisil. Evaporation of the solvent under reduced pressure left an orange oil, which was subjected to column chromatography on SiO_2 using hexane/ethyl acetate (10:1) as an eluent to give 0.340 g (0.98 mmol, 49% yield) of **12** (R = 2,6-xylyl) as a pale orange solid: mp 77–78 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.64 (s, 3 H), 1.68 (s, 3 H), 2.21 (s, 6 H), 2.32 (s, 6 H), 5.44 (s, 1 H), 5.96 (br s, NH), 6.90–7.07 (m, 4 H), 7.30–7.33 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 18.1, 18.3, 18.4, 97.9, 106.4, 123.0, 126.3, 127.5, 128.7, 133.6, 134.9, 136.5, 137.7, 144.3, 147.1, 153.0; IR (KBr) 3296 (NH), 1692 (C=N, C=CN), 1628 (C=CO) cm^{-1}. Anal. Calcd for $C_{23}H_{26}N_2O$: C, 79.73; H, 7.56; N, 8.09. Found: C, 79.77; H, 7.52; N, 8.06.

11a (R = *tert*-butyl): 26% yield; a pale orange solid; mp 70–72 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.32 (s, 9 H); 1.35 (s, 9 H), 1.76 (s, 3 H), 1.86 (s, 3 H), 4.36 (s, 1 H), 5.59 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.4, 18.1, 28.4, 30.0, 50.6, 53.4, 93.4; IR (KBr) 3396 (NH), 1698 (C=CN), 1672 (C=N), 1630 (C=CO) cm^{-1}. Anal. Calcd for $C_{15}H_{28}N_2O$: C, 71.96; H, 10.47; N, 11.19. Found: C, 71.79; H, 10.73; N, 11.14.

11c (R = 2,6-diethylphenyl): 54% yield; a pale orange solid; mp 83–84 °C (hexane); ^1H NMR ($CDCl_3$) δ 1.20 (t, J = 7.6 Hz, 6 H), 1.23 (t, J = 7.6 Hz, 6 H), 1.63 (s, 3 H), 1.65 (s, 3 H), 2.57 (q, J = 7.6 Hz, 4 H), 2.69 (q, J = 7.6 Hz, 4 H), 5.44 (s, 1 H), 5.97 (s, 1 H), 7.03–7.21 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 15.0, 17.4, 18.3, 24.9, 25.0, 97.5, 106.2, 123.3, 125.8, 126.9, 127.1, 134.5, 136.6, 137.5, 141.4, 143.4, 147.2, 153.1; IR (KBr) 3384 (NH), 1702 (C=N), 1676 (C=CN), 1634 (C=CO) cm^{-1}. Anal. Calcd for $C_{26}H_{30}N_2O$: C, 80.79; H, 7.82; N, 7.25. Found: C, 80.60; H, 7.84; N, 7.20.

General Procedure for the Pd-Catalyzed Reaction of 1a with Heterocumurenes. 4,4-Dimethyl-5-methylene-3-phenyloxazolidin-2-one (12a). In a flame-dried 10-mL two-necked flask fitted with a condenser and rubber septum were placed $Pd(PPh_3)_4$ (0.115 g, 0.1 mmol) and a magnetic stirring bar under nitrogen. To the vessel were successively added toluene (3 mL), a solution of **1a** (0.256 g, 2.0 mmol), and phenyl isocyanate (0.262 g, 2.2 mmol) in toluene (2 mL) by a syringe. The solution was stirred at reflux temperature for 8 h. After cooling, the mixture was filtered with Florisil. Evaporation of the solvent in reduced pressure left an orange oil, which was subjected to column chromatography on SiO_2 using hexane/ethyl acetate (5:1) as an eluent to give 0.317 g (1.56 mmol, 78% yield) of 4,4-dimethyl-5-methylene-3-phenyloxazolidin-2-one as a major product and 4,4-dimethyl-5-methylene-1,3-diphenylimidazolidin-2-one as a minor product.

4,4-Dimethyl-5-methylene-3-phenyloxazolidin-2-one (12a): 78% yield; a white solid; mp 121–122 °C; ^1H NMR ($CDCl_3$) δ 1.46 (s, 6 H), 4.33(d, J = 3.4 Hz, 1 H), 4.76 (d, J = 3.4 Hz, 1

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H), 7.2–7.5 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 28.2, 63.2, 84.5, 128.6, 129.2, 129.4, 134.0, 153.7, 160.6; IR (KBr) 1780 (C=O), 1678 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.84; H, 6.43; N, 6.92.

4,4-Dimethyl-5-methylene-3-(4-methylphenyl)oxazolidin-2-one (12b): 79% yield; a white solid; mp 102–104 °C; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 6 H), 2.38 (s, 3 H), 4.32 (d, J = 3.0 Hz, 1 H), 4.75 (d, J = 3.0 Hz, 1 H), 7.12 (d, J = 9.0 Hz, 2 H), 7.24 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.1, 28.1, 63.0, 84.5, 129.0, 130.1, 131.1, 138.8, 153.8, 160.7; IR (KBr) 1780 (C=O), 1680 (C=C) cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 72.07; H, 6.99; N, 6.58.

4,4-Dimethyl-5-methylene-3-(4-methoxyphenyl)oxazolidin-2-one (12c): 64% yield; a white solid; mp 123–124 °C; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 6 H), 3.83 (s, 3 H), 4.32 (d, J = 3.0 Hz, 1 H), 4.75 (d, J = 3.0 Hz, 1 H), 6.95 (d, J = 9.2 Hz, 2 H), 7.16 (d, J = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.0, 55.5, 62.9, 84.5, 114.7, 126.2, 130.6, 153.9, 159.7, 160.6; IR (KBr) 1775 (C=O), 1665 (C=C). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.01. Found: C, 66.83; H, 6.49; N, 5.94.

4,4-Dimethyl-5-methylene-3-(4-chlorophenyl)oxazolidin-2-one (12d): 58% yield; a white solid; mp 118–119 °C; ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 6 H), 4.35 (d, J = 3.2 Hz, 1 H), 4.77 (d, J = 3.2 Hz, 1 H), 7.20 (d, J = 8.6 Hz, 2 H), 7.42 (d, J = 8.6 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.1, 63.2, 84.9, 129.7, 130.3, 132.5, 134.7, 153.5, 160.2; IR (KBr) 1785 (C=O), 1679 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_{12}NO_2Cl$: C, 60.64; H, 5.09; N, 5.89; Cl, 14.92. Found: C, 60.41; H, 5.12; N, 5.79; Cl, 14.94.

4,4-Dimethyl-5-methylene-3-(4-nitrophenyl)oxazolidin-2-one (12e): 90% yield; an orange solid; mp 170–172 °C; ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 6 H), 4.41 (d, J = 3.5 Hz, 1 H), 4.83 (d, J = 3.5 Hz, 1 H), 7.52 (d, J = 9.2 Hz, 2 H), 8.31 (d, J. = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.1, 63.8, 85.5, 124.8, 128.1, 140.7, 146.7, 152.9, 159.7; IR (KBr) 1768 (C=O), 1680 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 57.80; H, 4.73; N, 11.63.

4-Methyl-5-methylene-3,4-diphenyloxazolidin-2-one (12f): 33% yield; a white solid; 144–145 °C; ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 3 H), 4.15 (d, J = 3.5 Hz, 1 H), 4.80 (d, J = 3.5 Hz, 1 H), 6.8–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 24.6, 67.9, 84.5, 125.8, 126.3, 126.6, 127.5, 128.6, 128.7, 128.9, 129.0, 134.5, 141.8, 160.4; IR (KBr) 1785 (C=O), 1680 (C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.82; H, 5.66; N, 5.24.

4-(3-Butenyl)-4-methyl-5-methylene-3-phenyloxazolidin-2-one (12g): 66% yield; a white solid; mp 61–63 °C; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 3 H), 1.66 (ddd, J = 7.1, 9.0, 14.2 Hz, 1 H), 1.80 (ddd, J = 6.2, 9.9, 14.2 Hz, 1 H), 2.23 (m, 2 H), 4.31 (d, J = 3.5 Hz, 1 H), 4.83 (d, J = 3.5 Hz, 1 H), 5.00 (ddt, J = 1.6, 1.6, 10.4 Hz, 1 H), 5.05 (ddt, J = 1.6, 1.6, 17.0 Hz, 1 H), 5.79 (ddt, J = 6.2, 10.4, 17.0, 1 H), 7.23–7.48 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.7, 27.9, 39.0, 66.4, 85.2, 115.4, 128.3, 128.4, 129.5, 134.0, 136.6, 153.9, 158.4; IR (KBr) 1780 (C=O), 1689 (C=C) cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.86; H, 7.06; N, 5.67.

4,4-Dimethyl-5-methylene-3-phenyl-2-(phenylimino)oxazolidine (14): 68% yield; a pale yellow solid; mp 96–99 °C; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 6 H), 4.26 (d, J = 3.2 Hz, 1 H), 4.66 (d, J = 3.2 Hz, 1 H), 6.97–7.44 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 28.2, 62.7, 83.4, 122.3, 123.6, 127.8, 128.3, 129.2, 129.7, 135.9, 148.6, 162.4; IR (KBr) 1720 (C=N), 1668 (C=C) cm^{-1}. Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.96; H, 6.52; N, 9.94.

4,4-Dimethyl-5-methylene-2-(diphenylmethylene)-1,3-dioxolane (15): 44% yield; a white solid; mp 92–93 °C; ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 6 H), 4.09 (d, J = 3.2 Hz, 1 H), 4.53 (d, J = 3.2 Hz, 1 H), 7.0–7.31 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 27.2, 81.1, 83.3, 127.9, 128.0, 128.2, 129.5, 130.1, 138.5, 138.7, 160.9; IR (KBr) 1652 (C=C) cm^{-1}; exact mass for $C_{19}H_{18}O_2$ (M^+) calcd 278.1307, found 278.1316.

General Procedure for the Pd-Catalyzed Reaction of 1a with Silylated Nucleophiles. Synthesis of 17. In a flame-dried 10-mL two-necked flask fitted with a condenser and rubber septum were placed $Pd(PPh_3)_4$ (0.115 g, 0.1 mmol) and a magnetic stirring bar under nitrogen. To the vessel were successively added toluene (3 mL), a solution of **1a** (0.256 g, 2.0 mmol), and trimethylsilyl cyanide (0.218 g, 2.2 mmol) in toluene (2 mL) by a syringe. The solution was stirred at reflux temperature for 12 h. After cooling, the mixture was filtered through Celite. Evaporation of the solvent in reduced pressure left an orange oil, which was subjected to Kugelrohr distillation [bp 160 °C (1.0 mmHg)] to give 0.225 g (1.23 mmol, 62% yield) of 4-methyl-3-(trimethylsiloxy)-3-pentanitrile (**17**) as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9 H), 1.62 (s, 3 H), 1.65 (s, 3 H), 3.17 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.4, 18.1, 18.8, 21.6, 114.9, 117.0, 133.2; IR (neat) 2264 (CN), 1728 (C=C) cm^{-1}; exact mass for $C_9H_{17}NOSi$ (M^+) calcd 183.1080, found 183.1072.

Methyl 5-methyl-2,2-pentamethylene-4-(trimethylsiloxy)hexenoate (22): 32% yield; colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9 H), 1.23 (s, 6 H), 1.57 (br s, 10 H), 2.27 (s, 2 H), 3.65 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 0.7, 18.3, 19.5, 23.6, 28.7, 34.4, 43.5, 51.4, 89.4, 113.4, 141.1, 176.7; IR (neat) 1732 (C=O), 1678 (C=C) cm^{-1}. Anal. Calcd for $C_{16}H_{30}O_3Si$: C, 64.38; H, 10.13. Found: C, 64.46; H, 10.17.

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